Problem Set 11

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1)

$$\hbar\omega < E < 3\hbar\omega \tag{1}$$

$$\langle E \rangle = \frac{11}{6}\hbar\omega \tag{2}$$

We can use the following equation to solve for the different components of the wave function (it is a superposition of multiple).

$$E = \left(n + \frac{1}{2}\right)\hbar\omega \tag{3}$$

$$\begin{aligned} 1 &< n + \frac{1}{2} < 3 \\ 0.5 &< n < 2.5 \end{aligned} \tag{4}$$

So therefore $n \in \{1, 2\}$. We want to construct a superposition of two wave functions with $n = 1, 2$ so that the expectation value of the energy (using Hamiltonian) is $\frac{11}{6}\omega\hbar$.

$$\frac{11}{6} = A^2 1.5 + B^2 2.5 \tag{5}$$

We can't yet determine the coefficients (A, B), but with normalization we can.

$$\psi(x) = A\psi_1(x) + B\psi_2(x) \tag{6}$$

$$\begin{aligned} 1 &= A^2 \int_{-\infty}^{\infty} \psi_1^*(x)\psi_1(x)\,\mathrm{d}x + B^2 \int_{-\infty}^{\infty} \psi_2^*(x)\psi_2(x)\,\mathrm{d}x \\ \text{orthonormality} \implies \quad 1 &= A^2 + B^2 \end{aligned} \tag{7}$$

Now we can solve for A and B.

$$\begin{aligned} \frac{11}{6} &= 1.5A^2 + (1 - A^2)(2.5) \\ \frac{11}{6} &= 1.5A^2 + 2.5 - 2.5A^2 \\ 0 &= \left(2.5 - \frac{11}{6}\right) - A^2 \\ \implies \quad A &= \sqrt{\frac{2}{3}} \end{aligned} \tag{8}$$

$$
\begin{aligned}
B^2 &= 1 - A^2 \\
B^2 &= \frac{1}{3} \\
B &= \sqrt{\frac{1}{3}}
\end{aligned}
\tag{9}
$$

We can plug these coefficients into the known solutions for the harmonic oscillator from the book.

$$
\psi(x) = \sqrt{\frac{2}{3}} \left(\frac{b}{2\sqrt{\pi}}\right)^{\frac{1}{2}} (2bx) e^{-\frac{1}{2}b^2x^2} + \sqrt{\frac{1}{3}} \left(\frac{b}{8\sqrt{\pi}}\right)^{\frac{1}{2}} (4b^2x^2 - 2) e^{-\frac{1}{2}b^2x^2}
\tag{10}
$$

2)

2.a)

$$
(n_x, n_y, n_z) = (5, 1, 1)
\tag{11}
$$

$$
5^2 + 1^2 + 1^2 = 27
\tag{12}
$$

So we need to find all possible combinations of three numbers so the sum of their squares equals 27.

Solutions:

$$
\begin{aligned}
&(5, 1, 1) \\
&(1, 5, 1) \\
&(1, 1, 5) \\
&(3, 3, 3)
\end{aligned}
\tag{13}
$$

2.b)

If one side (L_x) were to be increased by 5%, then we would have the following equation for the energy:

$$
E \propto \frac{n_x^2}{(1.05L)^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2}
\tag{14}
$$

For all of the previous combinations in Equation 13, there would now be 3 energy levels:

$(5, 1, 1)$ is no longer equal to $(1, 5, 1) = (1, 1, 5)$ because the first length is longer. $(3, 3, 3)$ also separates from the other two levels because of the length increase in the x dimension.

2.c)

2.d)

Yes, there still is degeneracy. To destroy it we would need to make all 3 lengths different (now 2 of them are still the same).

3)

$$\lambda = 450 \text{ nm} \tag{15}$$

$$E_{\text{photon}} = c\frac{h}{\lambda} \tag{16}$$

$$E = \frac{\pi^2\hbar^2}{2mL^2} \tag{17}$$

We can set Equation 17 and Equation 16 equal to each other and solve for the length (L). We know that because it is the lowest energy, we are transitioning from the case when one of the quantum numbers goes from $2 \to 1$ and the other 2 have a quantum number of 1.

$$\begin{aligned} c\frac{h}{\lambda} &= \frac{\pi^2\hbar^2}{2mL^2}(6-3) \\ L &= \sqrt{\frac{3\pi^2\hbar^2\lambda}{2mhc}} \\ L &= \sqrt{\frac{3\pi\hbar\lambda}{4mc}} \\ L &= \sqrt{\frac{3\pi\hbar(450 \times 10^{-9} \text{ m})}{4m_e c}} \end{aligned} \tag{18}$$

Plugging in for known values:

$$\begin{aligned} L &= 6.40 \times 10^{-10} \text{ m} \\ L &= 0.64 \text{ nm} \end{aligned} \tag{19}$$

4)

$$V(x,y,z) = \frac{1}{2}m\omega^2(x^2+y^2+z^2) \tag{20}$$

4.a)

$$\begin{aligned} H &= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 - \frac{\hbar^2}{2m}\frac{\partial}{\partial y^2} + \frac{1}{2}m\omega^2 y^2 - \frac{\hbar^2}{2m}\frac{\partial}{\partial z^2} + \frac{1}{2}m\omega^2 z^2 \\ &= -\frac{\hbar^2}{2m}\left[\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right] + \frac{1}{2}m\omega^2\left[x^2 + y^2 + z^2\right] \end{aligned} \tag{21}$$

4.b)

$$\psi(x,y,z) = \psi_1(x)\psi_2(y)\psi_3(z) \tag{22}$$

$$\begin{aligned} \hat{H}\psi(x,y,z) &= \hat{H}\psi_1(x)\psi_2(y)\psi_3(z) \\ &= \left[-\frac{\hbar^2}{2m}\psi_1''(x) + \frac{1}{2}m\omega^2 x^2\psi_1(x)\right]\psi_2(y)\psi_3(z) \\ &+ \left[-\frac{\hbar^2}{2m}\psi_2''(y) + \frac{1}{2}m\omega^2 y^2\psi_2(y)\right]\psi_1(x)\psi_3(z) \\ &+ \left[-\frac{\hbar^2}{2m}\psi_3''(z) + \frac{1}{2}m\omega^2 z^2\psi_3(z)\right]\psi_1(x)\psi_2(y) \end{aligned} \tag{23}$$

We can divide by $\psi_1\psi_2\psi_3$:

$$E = \underbrace{\left[-\frac{\hbar^2}{2m}\frac{\psi_1''(x)}{\psi_1(x)} + \frac{1}{2}m\omega^2 x^2\right]}_{E_1} + \underbrace{\left[-\frac{\hbar^2}{2m}\frac{\psi_2''(y)}{\psi_2(y)} + \frac{1}{2}m\omega^2 y^2\right]}_{E_2} + \underbrace{\left[-\frac{\hbar^2}{2m}\frac{\psi_3''(z)}{\psi_3(z)} + \frac{1}{2}m\omega^2 z^2\right]}_{E_3} \tag{24}$$

Each of these three terms has a unique energy that only depends on the dimension that they are a function of.

$$\begin{aligned} E_1 &= \hbar\omega\left(n_1 + \frac{1}{2}\right) \\ E_2 &= \hbar\omega\left(n_2 + \frac{1}{2}\right) \\ E_3 &= \hbar\omega\left(n_3 + \frac{1}{2}\right) \end{aligned} \tag{25}$$

4.c)

The ground state is when $n_1 = n_2 = n_3 = 0$.

$$\begin{aligned} E &= \hbar\omega\left(\frac{3}{2}\right) \\ &= \frac{3}{2}\hbar\omega \end{aligned} \tag{26}$$

$$\left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{1}{2}b^2x^2} + \left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{1}{2}b^2y^2} + \left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{1}{2}b^2z^2} \tag{27}$$

4.d)

The first excited state is when two of the quantum numbers are 0 and the other one is 1. There are three degenerate states because the ω is the same for all three dimensions.

We will solve for the energy when $n_1 = 1, n_2 = n_3 = 0$

$$\begin{aligned} E &= \hbar\omega\left(\frac{3}{2} + \frac{1}{2} + \frac{1}{2}\right) \\ &= \frac{5}{2}\hbar\omega \end{aligned} \tag{28}$$

Below is for the $(1, 0, 0)$ state, but all of the other states will look the same except that the x, y, z variables will be swapped.

$$\left(\frac{b}{2\sqrt{\pi}}\right)^{\frac{1}{2}}(2bx)e^{-\frac{1}{2}b^2x^2}\left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}}e^{-\frac{1}{2}b^2y^2}\left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}}e^{-\frac{1}{2}b^2z^2} \tag{29}$$

$(0, 1, 0)$:

$$\left(\frac{b}{2\sqrt{\pi}}\right)^{\frac{1}{2}}(2by)e^{-\frac{1}{2}b^2y^2}\left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}}e^{-\frac{1}{2}b^2z^2}\left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}}e^{-\frac{1}{2}b^2x^2} \tag{30}$$

$(0, 0, 1)$:

$$\left(\frac{b}{2\sqrt{\pi}}\right)^{\frac{1}{2}}(2bz)e^{-\frac{1}{2}b^2z^2}\left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}}e^{-\frac{1}{2}b^2y^2}\left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}}e^{-\frac{1}{2}b^2x^2} \tag{31}$$

4.e)

$$\begin{aligned} E\psi = &-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right) + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\psi\right) + \frac{1}{r^2\sin^2\theta\left(\frac{\partial^2}{\partial\phi^2}\right)}\right] \\ &+\frac{1}{2}m\omega^2r^2(\sin^2(\theta)\sin^2(\phi) + \sin^2(\theta)\cos^2(\phi) + \cos^2(\theta)) \\ E\psi = &-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right) + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\psi\right) + \frac{1}{r^2\sin^2\theta\left(\frac{\partial^2}{\partial\phi^2}\right)}\right] \\ &\underbrace{+\frac{1}{2}m\omega^2r^2}_{\text{nice potential!}} \end{aligned} \tag{32}$$

4.f)

To convert the eigenfunctions to spherical coordinates, we can just plug in the definitions of x, y, z in terms of r, θ, ϕ:

Ground state:

$$\left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{1}{2}b^2r^2\sin^2\theta\cos^2\phi} \left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{1}{2}b^2r^2\sin^2\theta\sin^2\phi} \left(\frac{b}{\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{1}{2}b^2r^2\cos^2\theta} \\ \left(\frac{b}{\sqrt{\pi}}\right)^{\frac{3}{2}} e^{-\frac{3}{2}b^2r^2} \tag{33}$$

$(1, 0, 0)$:

$$\left(\frac{b}{2\sqrt{\pi}}\right)^{\frac{1}{2}} \left(\frac{b}{\sqrt{\pi}}\right)(2br\sin\theta\cos\phi)e^{-\frac{3}{2}b^2r^2} \tag{34}$$

$(0, 1, 0)$:

$$\left(\frac{b}{2\sqrt{\pi}}\right)^{\frac{1}{2}} \left(\frac{b}{\sqrt{\pi}}\right)(2br\sin\theta\sin\phi)e^{-\frac{3}{2}b^2r^2} \tag{35}$$

$(0, 0, 1)$:

$$\left(\frac{b}{2\sqrt{\pi}}\right)^{\frac{1}{2}} \left(\frac{b}{\sqrt{\pi}}\right)(2br\cos\theta)e^{-\frac{3}{2}b^2r^2} \tag{36}$$

5)

$$\Psi(r, \theta, \phi) = Af(r)\sin\theta\cos\theta e^{i\phi} \tag{37}$$

5.a)

We know that m_l is the z component of the angular momentum. From our general equation of $\Phi(\phi) = e^{im_l\phi}$ and our given equation of $\Psi(\phi) = e^{i\phi}$, we can conclude that $m_l = 1$.

$$\begin{aligned} & L_z = m_l\hbar \\ \implies & L_z = \hbar \end{aligned} \tag{38}$$

5.b)

We know that $l \in \{-1, 0, 1\}$ but we do not know which.

$$\Theta(\theta) = \sin\theta\cos\theta \tag{39}$$

$$
\begin{aligned}
\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right) - C\sin^2\theta\Theta(\theta) &= m_l^2\Theta(\theta) \\
\sin\theta\frac{\partial}{\partial\theta}(\sin\theta(\cos^2(\theta)-\sin^2(\theta))) - C\sin^3(\theta)\cos\theta &= m_l^2\sin\theta\cos\theta \\
\sin\theta\frac{\partial}{\partial\theta}(\sin\theta\cos^2(\theta)-\sin\theta\sin^2(\theta)) - C\sin^3(\theta)\cos(\theta) &= m_l^2\sin\theta\cos\theta \\
\cos^3(\theta) - 2\cos\theta\sin^2(\theta) - 3\cos\theta\sin^2(\theta) - C\sin^2(\theta)\cos\theta &= m_l^2\cos\theta \\
\cos^2(\theta) - 2\sin^2(\theta) - 3\sin^2(\theta) - m_l^2 &= C\sin^2(\theta) \\
\cos^2(\theta) - 5\sin^2(\theta) - 1 &= C\sin^2(\theta) \\
\cot^2(\theta) - 5 - \csc^2(\theta) &= C \\
\implies \quad C &= -6
\end{aligned} \tag{40}
$$

$$
C \equiv -l(l+1) \tag{41}
$$

$$
\begin{aligned}
L^2 &= -C\hbar^2 \\
L^2 &= 6\hbar^2
\end{aligned} \tag{42}
$$

6)

6.a)

$$
\begin{aligned}
n &= 4 \\
l &= 3 \\
m &= 3
\end{aligned} \tag{43}
$$

$$
\psi_{4,3,3}(r,\theta,\phi) = R_{4,3}(r)Y_l^{m_l}(\theta,\phi) \tag{44}
$$

$$
R_{43} = c_0 r^3 e^{-\frac{r}{4}a_0} \tag{45}
$$

$$
Y_3^3(\theta,\phi) = \sqrt{\frac{35}{64\pi}}\sin^3(\theta)e^{3i\phi} \tag{46}
$$

Equation 46 comes from the book.

We need to normalize the radial component (the spherical part is already normalized).

$$
\begin{aligned}
1 &= c_0^2\int_0^\infty r^2 r^6 e^{-r/(2a_0)}\,\mathrm{d}r \\
\frac{1}{c_0^2} &= 2.1\times10^9 a_0^9 \\
\implies \quad c_0 &= \sqrt{\frac{1}{2.1\times10^7 a_0^9}}
\end{aligned} \tag{47}
$$

$$
\psi_{433}(r,\theta,\phi) = \sqrt{\frac{1}{2.1\times10^7 a_0^9}}r^3 e^{-r/(4a_0)}\sqrt{\frac{35}{64\pi}}\sin^3(\theta)e^{3i\phi} \tag{48}
$$

6.b)

$$\begin{aligned}\langle r\rangle &= c_0^2 \int_0^\infty r r^2 r^6 e^{-r/(2a_0)}\,\mathrm{d}r \\ &= \frac{1}{2.1\times 10^7 a_0^9} 3.7\times 10^8 a_0^{10} \\ &= 18a_0\end{aligned} \tag{49}$$

This value makes sense because the electron is 4 times as far away, so the energy is about 4^2 as much as it would be in the ground state.

6.c)

$$\begin{aligned}|L| &= \sqrt{l(l+1)}\hbar \\ L^2 &= l(l+1)\hbar^2\end{aligned} \tag{50}$$

We know that the operator for the z component of the angular momentum is

$$\widehat{L_z}^2 = \frac{\partial^2}{\partial\phi^2}\hbar^2 \tag{51}$$

We can apply this to the wave function to find the eigenvalue which corresponds to the z component of the angular momentum.

$$\widehat{L_z}^2 e^{3i\phi} = \underbrace{-9}_{L_z^2} e^{3i\phi} \tag{52}$$

We know that $L^2 - L_z^2$ will give us the sum of the x and y components.

$$\begin{aligned}L^2 - L_z^2 &= L_x^2 + L_y^2 \\ (12+9)\hbar^2 &= \\ 21\hbar^2 &= L_x^2 + L_y^2\end{aligned} \tag{53}$$

7)

7.a)

$$P(r_1 < r < r_2) = \int_{r_1}^{r_2} R^*(r)R(r)r^2\,\mathrm{d}r \tag{54}$$

7.b)

$$R_{10}(r) = c_0 e^{-r/a_0} \tag{55}$$

We can normalize to find c_0:

$$
\begin{aligned}
\frac{1}{c_0^2} &= \int_0^\infty r^2 e^{-2r/a_0} \,\mathrm{d}r \\
\frac{1}{c_0^2} &= \frac{a_0^3}{4} \\
c_0 &= \frac{2}{\sqrt{a_0^3}}
\end{aligned}
\tag{56}
$$

$$
\begin{aligned}
P(r < 10^{-15} \ \ \mathrm{m}) &= \int_0^{10^{-15}} \frac{4}{a_0^3} e^{-2r/a_0} r^2 \,\mathrm{d}r \\
&\approx \frac{4}{a_0^3} \frac{\left(10^{-15}\right)^3}{3} \\
&\approx 9 \times 10^{-15}
\end{aligned}
\tag{57}
$$

We can also see that the exponential term will contribute very little to the integral at such small values of r, so it makes sense that the solution is on the same order at the radius of the nucleus.

So basically a zero probability, which makes sense… The electron should not be *inside* of the proton.

7.c)

$$
R_{21} = c_0 r e^{-r/(2a_0)}
\tag{58}
$$

We can normalize the radial part:

$$
\begin{aligned}
\frac{1}{c_0^2} &= \int_0^\infty r^4 e^{-r/a_0} \,\mathrm{d}r \\
\frac{1}{c_0^2} &= 24 a_0^5 \\
c_0 &= \frac{1}{\sqrt{24 a_0^5}}
\end{aligned}
\tag{59}
$$

Now we can calculate the probability of the electron being inside of the nucleus.

$$
\begin{aligned}
P(r < 10^{-15} \ \mathrm{m}) &= \int_0^{10^{-15}} \frac{1}{24 a_0^5} r^4 e^{-r/a_0} \\
&\approx \frac{\left(10^{-15}\right)^5}{5} \frac{1}{24 a_0^5} \\
&\approx 2 \times 10^{-26}
\end{aligned}
\tag{60}
$$

This is smaller than the ground state, which makes sense because it has more energy and therefore will spend more of its time further from the nucleus. The higher orbitals are, well higher, so less probability to be close to the nucleus.